

FLUCIRONITROSO COMPOUNDS:  
SYNTHESIS AND REACTIONS

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## INTRODUCTION

In 1954 a research project was established at the University of Florida for the purpose of developing elastomers which are thermally stable, flexible at low temperatures, and resistant to swelling in a variety of solvents.

Hammett (9, 10, 12, 13, 16, 17, 18, 20) has reported that fluorination can be equated with diacetylenation compounds, for example:



The analogue of tetrafluoroethylene and difluorodiacetylene remains flexible at  $-90^\circ$ , is unaffected over long periods at  $200^\circ$  in the presence of air, and does not burn. It is insoluble in common organic solvents and is unaffected by either hot concentrated sulfuric acid or hot concentrated aqueous potassium hydroxide (9, 11). These findings have prompted a more thorough investigation of diacetylenic nitrogen compounds.

The first synthesis of a nitrogen compound was reported nearly years ago by Baeyer (4, 5), but not until thirty years later was the first diacetylenic nitrogen compound prepared. Haer and Hesse (14) obtained a low yield of trifluorodiacetylene by treating silver cyanide with chlorine. The silver presumably arose from the silver chloride present in the cyanide as an impurity.

After another fifteen years had passed, Rosenblum and Katz (11) prepared trifluoroacetates by irradiating a mixture of bromofluoroethanes and nitric oxide in the presence of mercury which removes the iodine also liberated and provides with any chlorine chloride formed:



Other fluoroalkyl iodides have been converted to the corresponding nitrox compounds via this reaction (12, 13, 14, 15), and the reaction has also been demonstrated to be applicable to unsaturated systems. From Reaction (11) was able to obtain trifluoroacetates, although in yields of only 1 to 3 per cent. Rosenblum, Tarrant and Barry (16) allowed nitric oxide to react with perfluorooctyl iodide and with 2-bromotetrafluorooctyl iodide and obtained the corresponding unsaturated nitrox compounds in yields as high as 30 per cent and 18.3 per cent respectively.

Although the reaction of iodides with nitric oxide has been shown to be a rather simple route to a wide variety of nitrox compounds, it is nevertheless not a good preparative method. Fluoroalkyl iodides are relatively expensive, and while the yields of nitrox compounds which have been reported are generally high, the conversions are rather low. Furthermore, the reaction is carried out here only on a small scale and at pressures below one atmosphere. From Reaction (11) has published the most papers on this type of reaction, while (17) that, while the reaction of trifluoroethanethanes with nitric oxide is a simple route to trifluoroacetates, large quantities of this compound are best prepared from silver trifluoroacetate.

Banks (2) and Rasmussen (30) have reported that the pyrolysis of a mixture of aluminum chloride and silver trifluoroacetate (or heptafluoroborate), after the removal of excess aluminum chloride, gave the corresponding silver compound:



The formation of a large number of by-products reduced the yield of the desired silver compound to 15 to 18 per cent. In the reaction, there was obtained, in addition to trifluoroacrylonitrile, tetrafluoroacrylonitrile, chlorotrifluoroacrylonitrile, and hexafluoroacrylonitrile. Substantial improvements in the process have been reported by Banks, Rasmussen, and Holmstedt (31) and by Taylor, Brown, and Shaw (32). By purifying the aluminum acid chloride before the pyrolysis step, the first group of workers were able to obtain heptafluoroacrylonitrile in 45 per cent yield (30% conversion). In essentially the same way the acetal group prepared trifluoroacrylonitrile in an overall yield of 30 to 55 per cent.

Since it has been reported that the silver salts of the other polyfluoroacrylonitrile acids react with aluminum chloride to form acid chlorides (33), it would appear that the pyrolysis of these materials is a general and useful means of preparing fluorine-containing silver compounds. However, since the pyrolysis is carried out best at 150° to 200°, considerable care must be used, at temperatures above 150°

polysiloxane nitrates can be violently explosive. Their hydration analogues will explode even under mild heating (18).

Torrens and O'Donnor (14) recently developed a useful method for preparing disubstituted nitrate esters. Mercury fluoride is first added to a chlorosilane and the mercury dihalide obtained is reacted with nitrooxy silanes:



The net effect of the two-step reaction is the addition of nitrooxy fluoride to chlorosilanes. Unfortunately, however, the method appears to be limited since mercury fluoride has been successfully added only to 1,2-dichlorosilanes.

Several other workers have reported on the direct addition of nitrooxy fluorides to chlorosilanes (1, 2, 12, 13). Octafluorooctanoic acids very readily do give 70 to 100 per cent yields of 1-octfluorooctyl chlorosilanes (4, 13). Other esters, however, either do not yield nitrooxy compounds or yield only small amounts. Thus, with the one exception, the method is not suitable for the preparation of fluorosiloxane compounds.

A similar method involves addition of nitrooxy silanes to olefins. The addition to hydrocarbon olefins to obtain a siloxane-containing nitrooxy compound has been known for many years (19) and has been of some considerable importance in determining the structure of terpenes. However, until recently the method has not been successful for the preparation of fluorosiloxane-containing nitroxy compounds. Early workers (4, 12, 15, 16, 17, 18) found that the addition of nitrooxy silanes to fluorolefins did not occur readily and that high temperatures (ca 200°) or





difficulties are encountered due to blowups in the tubes when the reaction is run on a large scale (10).

The addition of nitric oxide to chlorine in the presence of ultraviolet light has not yet yielded an  $\alpha,\beta$ -disubstituted compound as many workers have hoped. It has been suggested (11) that nitric oxide alone has no effect on the reaction mixture and that the initial attack is by nitrogen dioxide. Some nitrogen dioxide is probably present even in purified nitric oxide and may also be generated during the reaction. The result is that a nitrochlorine derivative is produced (14, 15), for example



This same product can also be obtained from the direct addition of dinitrogen tetroxide to chlorine in the absence of light (16).

Although it is not of such significance, it is nevertheless interesting to note that the addition of nitrogen dioxide to chlorine compounds leads to the formation of nitric compounds. Usually the product is a mixture of the chlorite and nitrochlorite derivatives (17, 18, 19, 20). However, in the case of nitrochlorine, nitroxy chloride addition products can also be obtained (20):



Recently, Broder, Barton, and Taylor (21) have prepared perfluoromethanes by substitution of perfluoromethanes



Similar reactions have been used for the preparation of non-fluorinated aromatic nitro compounds [82].

Brayner and Binkovici [83] have reported that trifluoromethoxybenzenes can be prepared by the thermal decomposition of trifluoromethylhydrazine acid<sup>10</sup>:



A number of other methods for the formation of nitro compounds have been reported but, in general, seem to have no practical, preparative importance. A few such examples are the nitrochlorination of mixtures of nitric acids with *para*-trifluoromethyl aniline, trifluoromethyl iodide [84], or *para*-difluoromethyl aniline [85]:



Table 3 lists data on fluoromethylhydrazine compounds reported in the literature up to the present time [186].

TABLE I

## Ketone compounds

Isolated Formula	Standard Formula	Yield	Total no. mol. (molecules/l.)	$\log_{10} \frac{K_p}{K_p^0}$ (l./g. mol.)	$\Delta \log_{10} \frac{K_p}{K_p^0}$	Reference
$\text{C}_6\text{H}_5\text{CO}$	$\text{C}_6\text{H}_5\text{CO}$	1	50 (10)	20-21		25
$\text{C}_6\text{H}_5\text{CO}$	$\text{C}_6\text{H}_5\text{CO}$	1	50 (10)	21-23		26
$\text{C}_6\text{H}_5\text{CO}$	$\text{C}_6\text{H}_5\text{CO}$	2		26 (2125-6)		27
		1	75 (10)	26		28
		2	2-4	26		29
		4	20 (20)	25.5		4
		1	40	25.6		7
		4	150-400			33
		4	16	26		30
		1	1-7	25.7		31, 32
$\text{C}_6\text{H}_5\text{CO}$	$\text{C}_6\text{H}_5\text{CO}$	2		14-15		34
$\text{C}_6\text{H}_5\text{CO}$	$\text{C}_6\text{H}_5\text{CO}$	2	50	25		35
$\text{C}_6\text{H}_5\text{CO}$	$\text{C}_6\text{H}_5\text{CO}$	2	20 (10)	15		36

TABLE 3 (continued)

Reported Formula	Postulated Formula	Refined (percentage %)	$\lambda_{\text{max}}$ ( $\mu$ , m)	$\nu_{\text{max}}$ ( $\text{cm}^{-1}$ )	$d_{\text{max}}$	$d_{\text{min}}$
$\text{C}_{12}\text{H}_{18}\text{O}_2$	$\text{CH}_3(\text{CH}_2)_9\text{CO}_2\text{CH}_3$	3	20.5 (10)			40
$\text{C}_{12}\text{H}_{20}\text{O}_2$	$\text{CH}_3(\text{CH}_2)_{10}\text{CO}_2\text{CH}_3$	4	—			40
	$\text{CH}_3(\text{CH}_2)_8\text{CH}=\text{CHCO}_2\text{CH}_3$	7	95.6			40
		8	71	—1750		40
		7	60 (31)	—		40
		5	36	—		20
$\text{C}_{12}\text{H}_{18}\text{O}_2$	$\text{CH}_3(\text{CH}_2)_9\text{CO}_2\text{CH}_3$	6	6	—		20
		10		1670	$1.30 \times 10^{-2}$	44
				18.5 (10)		
$\text{C}_{12}\text{H}_{18}\text{O}_2$	$\text{CH}_3(\text{CH}_2)_9\text{CO}_2\text{CH}_3$	8	8	—	$1.30 \times 10^{-2}$	40
	$\text{CH}_3(\text{CH}_2)_8\text{CH}=\text{CHCO}_2\text{CH}_3$	4		1750		40
		5	36	—		20
		7	15			20
		10		20.7 (10)	$1.30 \times 10^{-2}$	44


Table 1. (Continued)

Explosion Formula	Structure Formula	Method	Yield per unit Concentration (%)	$\Delta G_{\text{exp}}$ (kJ/mole)	$\Delta G_{\text{cal}}$	$\Delta G_{\text{exp}}$	Reference
$\text{C}_2\text{H}_2\text{F}_2\text{O}$	$\text{C}_2\text{H}_2\text{F}_2\text{O}$	8	96	94.3/102	$1.34 \times 10^3$	$1.9 \times 10^3$	10
		7	82				
		6		16.3/102	$1.34 \times 10^3$	$1.3 \times 10^3$	10
		12	8.3	14.4/100			10
$\text{C}_2\text{H}_2\text{F}_2\text{Cl}_2$	$\text{C}_2\text{H}_2\text{F}_2\text{Cl}_2$	8		46.3			10
		5	46	50		$1.03 \times 10^3$	10
		20	30	40		$1.03 \times 10^3$	10
		10		64.3			10
		10		56.3-63.3			10
$\text{C}_2\text{H}_2\text{F}_2\text{O}$	$\text{C}_2\text{H}_2\text{F}_2\text{O}$	6	2.4	16.3-26.3/102	$1.34 \times 10^3$	$1.3 \times 10^3$	10
		10		—10 to —40			10
		1	87	463.7			11
		3	86 (1.0)	—32			10

TABLE 1 (Continued)

Exptl mol Formula	Deposited formula	Period	Total per unit (arbitrary H)	Age, years (H, $\pm$ 10%)	$d_p^1$	$d_p^2$	Reference
$\text{C}_2\text{F}_2\text{O}_2$	$\text{CF}_2\text{OOCF}_2\text{O}$	1	84.3				24
$\text{C}_2\text{F}_2\text{F}_2\text{O}_2$	$\text{CF}_2\text{FOCF}_2\text{F}_2\text{O}$	11		84-2400	1,300	1,300	45
$\text{C}_2\text{F}_2\text{O}$	$\text{CF}_2\text{OCF}_2\text{O}$	1	36	14.7			24
$\text{C}_2\text{F}_2\text{O}$	$\text{CF}_2\text{OCF}_2\text{O}$	1	40	-14.5 (-13.5)			8
$\text{C}_2\text{F}_2\text{O}$	$\text{CF}_2\text{OCF}_2\text{O}$	1	60 (100)	-12			16
		1	75	-14.5			7
		4	12.5	-14.5			10
		4	85 (100)	-16.7			1
		1	48	-16.7			11
	$(\text{CF}_2\text{O})_n$	6		-17			15
		11		-17			22
		15	1	-17 to -15			1
$\text{C}_2\text{F}_2\text{F}_2\text{O}_2$	$\text{CF}_2\text{FOCF}_2\text{F}_2\text{O}$	10		4000	1,300 <sup>a</sup>	1,400 <sup>b</sup>	7
		11		15-24		1,400 <sup>b</sup>	22

TABLE I (Continued)

Empirical formula	Structure formula	moles	Yield per cent (calculated %)	bp, °C/mm Hg	$n_D^{20}$	$d_4^{20}$	Reference
$C_{10}H_{12}O$	$CH_3(CH_2)_5CH=CH_2$	1	65 (10)	16-17/0.5			16
	$CH_3(CH_2)_4CH=CHCH_3$	1	66 (10)	17-18			16
	$CH_3(CH_2)_3CH=CHCH_2CH_3$	10	50	18-19			2
		20	100	19		1.4630	27
$C_{11}H_{14}O$	$CH_3(CH_2)_6CH=CH_2$	1	75 (11)	18-19/0.5			16
				20/0.5 (color)			
$C_{11}H_{12}O$		10	48	19/0.5 (color)			15
$C_{11}H_{14}O$	$CH_3(CH_2)_5CH=CHCH_3$	1	76 (14)	19-20/0.5			16
				20/0.5 (color)			

16. *Revised*

1. the reaction of  $\alpha$ -olefin isomers and cyclic olefins to substituted alkenes
2. the reaction of  $\alpha$ -olefin isomers and cyclic olefins



## TABLE 1 (Continued)

Reaction

6. the reaction of  $\text{HNO}_3$  (aq) on iron sulfide and stannous chloride in the presence of  $\text{H}_2\text{O}$  (aq)
7. the reaction of  $\text{HNO}_3$  (aq) on stannous chloride in the presence of a mercury dipole and ultraviolet light
8. the reaction of  $\text{HNO}_3$  (aq) on stannous chloride in the presence of stannous chloride in the presence of stannous chloride
9. the reaction of  $\text{HNO}_3$  (aq) on stannous chloride in the presence of stannous chloride in the presence of stannous chloride
10. the reaction of  $\text{HNO}_3$  (aq) on stannous chloride in the presence of stannous chloride in the presence of stannous chloride
11. the reaction of  $\text{HNO}_3$  (aq) on stannous chloride in the presence of stannous chloride in the presence of stannous chloride
12. the reaction of  $\text{HNO}_3$  (aq) on stannous chloride in the presence of stannous chloride in the presence of stannous chloride
13. the oxidation of an iron-sulfur alloy

## Summary

Terpenes are relatively inexpensive and a fairly wide variety of them may be readily obtained. They are therefore considered as good starting materials for the preparation of ester fluorosynthesizing compounds, and a study was undertaken of ways to convert alkenes to esters conveniently. As has already been mentioned in the previous section of this dissertation, R. L. O'Connor, another worker in this laboratory, added acetic anhydride to 1,1-difluoroalkenes and then allowed the resulting alkyls with aluminum chloride to obtain various compounds (4), 30. The net result was the effective addition of aluminum chloride across the double bond,

It now seemed desirable to study further the addition of aluminum chloride to alkenes. Other workers have reported on this process (30, 38, 40), but a practical method suitable to large scale synthesis was not available. It also seemed desirable to find new routes to fluorosynthesizing esters and to study some of the reactions of these compounds.

### The Addition of Aluminum Chloride to Alkenes

In the initial work, a mixture of an alkene and aluminum chloride was irradiated by sunlight. The reaction proceeds by an initial cleavage of the C-H bond followed by an attack of the chlorine atom on the double bond. The intermediate chloroaluminum alkyl radical may then react with a second radical to produce the desired alkylated compound, or it

and 1,3-dichloro-2-nitrobenzoyl chloride (prepared as from 2-nitrobenzoic acid)



In the reaction illustrated with 2-nitrochlorobenzoyl chloride, about a 2% yield of nitro- and dichloro compounds was obtained. The nitro- and dichloro compounds arising along with the lowest 4% yield of the nitrobenzene (14), thus as 1,3-dichloro-2-nitrochlorobenzene was formed. With perchloroacetylene only 2-chloro-2-nitrochlorobenzene was produced.

A third major product which is formed in the reaction is a nitro compound. In their early attempts to react nitroaryl chlorides with 2-nitrochlorobenzoyl chloride, Friedman (12, 13) and Nicholson (14) found a material to which they assigned the structure 1,3-dichloro-2-nitrochlorobenzene. Park (14) has mentioned the results of these workers and reports that the nitro compound obtained is actually 1,3-dichloro-2-nitrochlorobenzene. This he shows arises from both the addition of nitro chloride and from the chloroacetylation of the nitro compound. O'Malley (15), in his studies of the chloroacetylation of 1,3-dichloro-2-nitrochlorobenzene, has indicated that the nitro compound produced is 1,3-dichloro-2-nitrochlorobenzene rather than the nitro ketone claimed by Park. This result has been now verified. Chloroacetylation gave 1,3-dichloro-2-nitrochlorobenzene was heated in a

which take as  $\text{C}_2\text{F}_5$  for two days. Analysis by nuclear magnetic resonance of the crude product obtained is to be exclusively 1,2-dichloro-1-methyl-2-methoxyethane. None of the isomer reported by Park was found.

It thus seems probable that the structure of the isomer proposed reported by both Rasmussen and Tolbert is correct. Their reactions were run at high temperatures, and any isomer product formed would have been rapidly disproportionated. The isomer product obtained from the reaction of methyl chloride and methoxychloroethylene is, in light, reported in this dissertation, was analyzed by nuclear magnetic resonance analysis and found to be a mixture of both isomers. Thus, the isomer material is apparently formed by both addition of methyl chloride and the disproportionation of the mixture proposed.



Table I lists some of the products obtained from the reaction of alkenes with methyl chloride in sunlight. It will be noticed that the reaction with trichloroethylene did not produce a hydrogen-containing isomer compound. The anticipated reaction was:



Lovins's rule (24) predicts that the attacking chlorine atom will add to the  $\text{CF}_3$  end of the olefin rather than the  $\text{CH}_2$  end. Rasmussen (24), however, has noted that  $\pi$ -bond attack equally occurs at both ends of this particular olefin. Thus, it seems not unlikely that the addition step in two reactions involves the formation of two different

Table 1

Products Observed in This Work from  
the Reaction of Chlorine with Nitrogen Dioxide in Benzene

Starting Material	Major Products Observed	Per Cent Conversion
$\text{Cl}_2/\text{NO}_2$	$\text{Cl}_2\text{NClNO}_2$	38
	$\text{Cl}_2\text{NClNO}_2$	15.2
	$\text{Cl}_2\text{NClNO}_2$	9
	$\text{Cl}_2\text{NCl}_2\text{NO}_2$	9
$\text{Cl}_2/\text{NO}_2/\text{O}_2$	$\text{Cl}_2\text{NClNO}_2$	27
	$\text{Cl}_2\text{NClNO}_2$	9.3
	$\text{Cl}_2\text{NClNO}_2$	
	$\text{Cl}_2\text{NO}_2$	
$\text{Cl}_2/\text{NO}_2/\text{O}_2/\text{O}_3$	$\text{Cl}_2\text{NClNO}_2/\text{Cl}_2\text{NO}_2$	19
	$\text{Cl}_2\text{NClNO}_2/\text{Cl}_2$	38
	$\text{Cl}_2\text{NClNO}_2/\text{Cl}_2/\text{O}_3$	46
$\text{Cl}_2/\text{NO}_2$	$\text{Cl}_2\text{NClNO}_2$	26
	$\text{Cl}_2\text{NClNO}_2$	2.4
	$\text{Cl}_2\text{NCl}_2\text{NO}_2$	14
	$\text{Cl}_2\text{NO}_2/\text{NO}_2/\text{O}_2$ (1)	
$\text{Cl}_2/\text{NO}_2$	$\text{Cl}_2\text{NClNO}_2$	14
	$\text{Cl}_2\text{NClNO}_2$	1.5
	$\text{Cl}_2\text{NClNO}_2$	8
	$\text{Cl}_2\text{NCl}_2\text{NO}_2/\text{O}_2$	1.5
	$\text{Cl}_2\text{NCl}_2$	
$\text{Cl}_2/\text{NO}_2/\text{O}_2$	$\text{Cl}_2\text{NClNO}_2/\text{O}_2$	12.4

Table 2 (continued)

Chloride	Super Factorial Studied	Per Cent Conversion
	$\text{OP}_2(\text{CH}_2\text{CH}_2)_2\text{I}_2$	21
$\text{OP}_2\text{HCl}_2$	$\text{OP}_2(\text{CH}_2\text{CH}_2)_2\text{O}$	



The primary allylic product can be explained in terms of radical (12):



The allylic product from the reaction of radical (13) was not observed (still) (quite is question).

The addition to 3-ethyl-3-methylpentene is an interesting problem since Leitch's rule predicts an almost equal probability of attack either on both  $\gamma$  terminal and central olefinic carbon atoms.

$\Delta H$  for  $\gamma$  is 8.5,  $\Delta H$  for  $\beta$  is 9.5. Although an attack on the central carbon atom seems to be slightly more preferred, the former side of 3-ethyl-3-methylpentene is the only side product seems to indicate that attack occurs more the attack to be at the terminal carbon.



Since no evidence of the formation of a nitroso compound was observed at any time during the reaction, it seems doubtful that the nitro compound arises from the oxidation of 3-ethyl-3-methylpentene primary.

The multiple addition of nitroethyl nitride to olefins is further complicated by formation of allyl nitrites, azo-nitrites, and polymers, and it is dangerous to run on a large scale. The sole use of nitroethyl

the reaction mixture. The reaction mixture is then poured into water and the solid product is filtered off and dried. The reaction mixture is then poured into water and the solid product is filtered off and dried. The reaction mixture is then poured into water and the solid product is filtered off and dried.

### Preparation of the reaction mixture

The reaction mixture is prepared by the addition of the reactants to the reaction vessel. The reaction mixture is then stirred for a period of time. The reaction mixture is then poured into water and the solid product is filtered off and dried. The reaction mixture is then poured into water and the solid product is filtered off and dried. The reaction mixture is then poured into water and the solid product is filtered off and dried.

The reaction mixture is prepared by the addition of the reactants to the reaction vessel. The reaction mixture is then stirred for a period of time. The reaction mixture is then poured into water and the solid product is filtered off and dried. The reaction mixture is then poured into water and the solid product is filtered off and dried. The reaction mixture is then poured into water and the solid product is filtered off and dried.



## EXPERIMENTAL SECTION

The first set of studies designed to determine whether silver chloride formed, but the results were rather disappointing. It was found that the reaction was reversible, whereas in  $\beta$ -hydroxyethyl ester the reaction went very largely to completion. Silver chloride was decomposed by nitroethyl chloride and was therefore ~~not~~ used as an insoluble solvent.

Aluminum chloride was not the only catalyst which was found to catalyze the reaction, but it was by far the best of those tested under identical conditions. It was about 1.4 times as effective as the next best catalyst found, which was lithium chloride. Lithium salts in general were found to catalyze the reaction in the order  $\text{LiCl} > \text{LiF} > \text{LiBr} > \text{LiI}$ . Aluminum bromide also was found to catalyze the reaction but appeared to give rise to nitroethyl bromide addition products as did lithium bromide.

Table I lists the results of a series of reactions between silver trifluoroacetate and nitroethyl chloride run under identical conditions in a continuous flow reactor using different catalysts. A high flow rate of the gaseous reactants was used so that a complete reaction would not be obtained even in the most reactive system. The ability of each material used to catalyze the reaction may be judged from the amount of nitroethyl chloride produced.

The nature of which the chlorine chloride functions has not been definitely determined, but evidence has been accumulated which points to give at least a partial picture of the reaction.

Four sealed tubes containing the following alcohols were shaken in the dark: (1) nitroethyl chloride, and silver trifluoroacetate; (2) nitroethyl chloride, silver trifluoroacetate, and aluminum chloride; (3)







which can catalyze the reaction. This was not observed. If an addition of aluminum can remove even the inhibition of aluminum chloride, there should just be no need for the presence of aluminum chloride, and it seems unlikely that aluminum tetrahaloalkanoates would break up to give a chloride ion.



This lithium salt in general appears to catalyze the reaction in close concert with an attack by some species other than a chloride ion alone.

An alternate mechanism which may apply is essentially that of the well-known Friedel-Crafts addition of aryl halides to alkenes. It would involve the following steps.



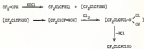
However, as a consequence of low ionizability of chlorine, the electron density at the double bond in chlorinated alkenes is decreased, so that electrophilic addition becomes more difficult while nucleophilic addition becomes easier. In fact, Miller (11) has only recently reported the first example of an electrophilic addition to a chlorinated alkene which occurs via fluorine and which occurs across the double bond. Thus it does not seem probable that the initial attack is by the electrophilic ion. Also, a number of attempts have been to add aluminum chloride to chlorinated alkyl tetrafluoroalkanoates.



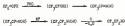


which would not be present in the gig compound. Assuming that all other factors are equal, the ground state of the gig cation should therefore be at a slightly higher energy level than that of the gagg cation, and the difference between the ground state and the transition should be less for the gig cation.

Trifluoromethylphenyl reacted to yield 1,3-dichloro-6-methylacetofluorobenzene and 1,3-dichloro-6-fluorobenzene, and the following reaction path is suggested:



It is of interest to note that compounds (C)<sup>1</sup> found trifluoromethylphenyl to react with nitrolyl fluoride to form pentafluorobenzonitrile and pentafluorobenzene. He has proposed the following reaction sequence:



An analogous path may also be written for the reaction with nitrolyl chloride, and it is difficult to distinguish this from the path already suggested.

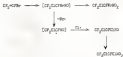
O'Connor (13) showed gag-(1,3,4,5-tetrafluorophenyl) reacting with nitrolyl chloride and obtained 1-chloro-6-methylacetofluorobenzene,



1,3-dichloro-2-trifluoromethylbenzene, and 1-chloro-2-trifluoromethylbenzene.

It is suggested that the first two products are formed by a free radical displacement of hydrogen by chlorine before the second step is allowed. However, it is interesting to note that he did not observe a free radical displacement of bromine by chlorine when he attempted to cleave  $\text{Hg}(\text{O}-\text{trifluoromethyl})_2$  mercury with nitroethyl chloride. Yet it seems that bromine would be more readily displaced by chlorine than would hydrogen, and if his suggested explanation were correct, he should have obtained similar results with  $\text{Hg}(\text{O}-1,3,5\text{-trifluoromethyl})_2$  mercury.

Bromine/trifluoromethylbenzene also reacted to yield 1,3-dichloro-2-trifluoromethylbenzene along with 1,3-dichloro-2-bromotrifluoromethylbenzene and 1-bromo-2-trifluoromethylbenzene. This reaction may be readily explained by the following sequence:

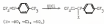


The radical  $[\text{C}_6\text{H}_4\text{CBr}]$  has been proposed as an intermediate in the disproportionation of 1,3-dichloro-2-trifluoromethylbenzene (5).

Bromotrifluorobenzene readily reacted to form 1-bromo-2-trifluoromethylbenzene while the relatively unreactive chlorine, 1,3-dichloro-2-trifluoromethylbenzene, bromotrifluorobenzene, and trichlorobenzene did

not react to form nitrous compounds, although some chlorination was observed.

*p*-Trifluoromethylbenzoyl fluoride readily reacted to produce the anticipated chloroacetone, dichloro, and chloroaceto-propylene:



Recently in this laboratory Ward Oliver [31] has successfully used the chlorine-chloride-dichloroformate system to prepare such nitrous compounds as 3-chloro-3-dichloro-2,2-dichloroethylchloroformate and 4-chloro-4,4,4-trichloro-2-chloro-2,2,2-trichloroethylchloroformate.

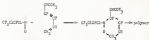
### The Synthesis of Nitro Compounds

It has been of considerable interest to find new routes to fluorinated nitro compounds. Of the number of possibilities which have been investigated, the most promising seems to be the reduction of nitro compounds. Nitro compounds are found as by-products in almost all preparations of nitrous compounds and also can be prepared independently by a variety of methods [32, 33, 34].

It is well known that hydrogen nitro compounds can be readily reduced to primary amines. With aromatic nitro compounds it is possible to isolate a number of intermediate reduction products in good yield by proper control of the reduction conditions, and nitrobenzene has been shown to be an intermediate reduction product of nitrobenzene [35]. It thus seemed reasonable to investigate the possible preparation of fluorinated nitro compounds from nitro compounds.



latter does react violently at 0°, and addition to it had to be carried out at -80°, however, on warming up the product rapidly polymerized yielding only a tar:



The reaction could be obtained with perfluorobutadiene or with 1,2-dichloro-6-chloropent-4-ene-type even under mild heating. That the latter gave no reaction is not surprising since a Markovnikov addition to it would necessitate the formation of a cyclic alkene. That perfluorobutadiene did not react indicates that the diene requires a terminal  $\text{HBr}$  group in order to undergo the reaction, and it is suggested that the initial attack is on the terminal double carbon that bears a hydrogen atom. This is in accord with Lovins's rule (10) since it is this carbon which has the lowest  $\Sigma$  ion value of the substituents.

It seems most probable that the reaction proceeds through an open-chain directed type of transition state, for example:

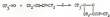


If the transition state had a cyclic delocalized (four centered) structure, the product should consist of two isomers:



This was not observed.

It is interesting to note that only a cis-oriented ring addition product was formed. Alkene compounds react with diazonium to yield *cis*-additions (10), but ~~an analogous~~ reaction with diazo was not observed.



or



This is not really too surprising if one considers the two possible diradical structures of the transition state proposed:



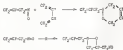
[A]



[B]

Lowman's rule (66) indicates that the radical groups  $\text{CF}_2\cdot$  and  $\cdot\text{CF}_3$  have approximately the same reactivity. However, steric considerations would obviously favor reaction through structure [A]. Some idea of the energy difference between the two structures may be gained by noting that, while nitroacetylene readily reacts with nitroacetylene at room temperature or below to form azides, the reaction with nitroacetylene to form azonitrides requires a temperature of about  $150^\circ$ .

As might be anticipated, trichloropentafluoroacetylene reacted rapidly with 1,1,2-trichloroethane to form an azide, but did not react with itself to yield an azonitride:



Quinone may be used for identification purposes. Thus, the alkyne isomer prepared from the reduction of 1,2-dichloro-1-trichloroethane was identified to be 1,2-dichloro-1-trichloropentafluoroacetylene by reacting it with 1,1,2-trichloroethane and comparing the infrared and nuclear magnetic resonance spectra of the product with those of an

crystalline sample of 2-[1,3-bis(trifluoromethyl)propyl]-3,3,3-trifluoro-2,4-dihydro-4H-pyran.

Crystalline with fluorine on both the ring and the side chain are fairly stable up to about 150° in the absence of air. It would seem that they might therefore be useful in microcapsule type equipment with such white or clear colors.



The first unit shown still possesses a double bond in the ring which may be a possible site for crosslinking if desired. The second has a  $\text{CF}_2\text{CFH}-$  group which perhaps can be dehalogenated under suitable conditions to yield a crosslinking site. If desired, reactions with functional groups on either the ring or the side chain may be synthesized.

It has been mentioned previously that an amine with a perfluorinated side chain was prepared successfully from the addition of  $\beta$ -chloroethylamine to 1,1,3-trifluoro-2-butene. Attempts were also made to prepare a derivative having a trifluoromethyl side chain. The addition of trifluoromethylacetylene to a diene could not be carried out since a suitable catalyst for the preparation of the diene compound was not available. Attempts to dehalogenate 1,3-dichloro-2-methylacetylene under a variety of conditions or to react other trifluoromethyl acetylene derivatives or  $\beta$ -trifluoromethyl amines with although alkenes resulted at best in the formation of a polymer. It was





Weak tarry polymers. Rings derived from addition to 1,1,2-trifluoro-2-methyl-2-butene were sticky.

A nuclear magnetic resonance study of pure, partially decomposed, and fully decomposed samples of 2-(1-chloro-2-methyl-2-propenyl)-3,3,4-trifluoro-2,5-dihydro-1,3-oxadiazole indicated that the decomposition involves the loss of fluorine from the  $=CF_2$  group in the ring. The infrared spectra of the decomposition material obtained from a number of samples having this ring all showed similar absorptions and identical peaks at  $1830\text{ cm}^{-1}$ . This may be accounted for by loss of fluorine from the  $=CF_2$  group to form either a carbonyl or an  $=C=O$  group.

Since the decompositions were carried out in glass tubes, silicon tetrafluoride was always one of the products as might be anticipated. This material was easily identifiable from its exceptionally strong infrared absorption at  $1830\text{ cm}^{-1}$ . Carbon dioxide was produced also and was easily identifiable by its unique infrared spectrum.

The nuclear magnetic resonance spectrum of the material obtained from the decomposition of 2-(1-chloro-2-methyl-2-propenyl)-3,3,4-trifluoro-2,5-dihydro-1,3-oxadiazole showed the formation of a rather unusual multiplet at  $-47.5\text{ cps}$ , relative to external trifluoroacetic acid which was split 1:1 quartet coupling into a doublet-doublet by 13.5 and 7.5 cps. The chemical shift is in the region of either a  $-COF$  group or an  $=CF_2$  group. A  $-COF$  group gives a sharp peak while an  $=CF_2$  group gives a rather broad one. Since the shape of the observed peak was midway between the two, it is difficult to say which of the two groups it represents. However, when an acetone solution of polymer beads was added to the decomposition material from any of the crosslinking rings derived from 1,1,2-trifluoro-2-methyl-2-butene, the solution immediately

forming a multi-layered, undulating, and fibrous of these layers. This will be a positive test for an alloy steel.

Unfortunately, up to the present time, the composite products have not been separated into their constituent components. This has been virtually because of the small amount of materials that have been available to work with. It does appear, however, that some interesting chemistry is involved here and that a detailed investigation of the decomposition of samples would be justified.

Infrared spectra were obtained using a Perkin-Elmer model 570 Grating Spectrophotometer. Nuclear magnetic resonance spectra were obtained by a Varian High Resolution Nuclear Magnetic Resonance Spectrometer, model A60 operating at 56.4 megacycles for determination of the carbon spectra and at 60 megacycles for determination of the proton spectra. The nuclear magnetic resonance spectra were interpreted by Dr. William E. Bach, Jr. and David Jones.

analytical super phase chromatographs were obtained using either a 10 foot x 4.00 inch column packed with a 4-14 mixture of dinonyl phthalate and dodecylcellulose "Fluoropak," 10/100 mesh size or an 8 foot x 4.00 inch column packed with a 4-10 mixture of Celitex and Decapag, 100. "Milesco Chloranil," 10/100 and "Chromasorb," 10/100 mesh size. Eluent was used as the carrier gas. Temperature scale separations were performed at either a 5 foot x 1.1 inch column packed with a 4-14 mixture of dinonyl phthalate and "Fluoropak," 10/100 mesh size or an 8 foot x 4.00 inch column packed with a 4-10 mixture of "Milesco Chloranil" and "Chromasorb," 10/100 mesh size. In runs not used as the carrier gas,

Elemental analysis of 3-allyl-8-oxabicyclo[3.2.1]oct-2-ene was performed by Laboratory<sup>2</sup> Kharayutskaya Laboratory. See Table: element analysis, was performed by the author, all other analyses were performed by Laboratory<sup>2</sup> Kharayutskaya Laboratory.

The affected animals are 2-year-old and 3-year-old females, with

heated in a vacuum system constructed by Dr. John Hurry. Molecular weights were determined by Rastaldi's method, and boiling points were determined independently when indicated. Conversions are based upon the total amount of starting material used for a reaction. Yields are based only upon the amount of starting material consumed in a reaction.

#### The Addition of Nitrogen Oxides to Olefins in the Presence of Boric Acid

In general, the reaction flask was swept out with nitrogen, evacuated, and then filled with equal molar amounts of nitrogen chloride and olefin. After several hours of irradiation, the products were either pumped out or swept out with nitrogen. Products were separated by preparative scale gas chromatography.

1,4-Addition to dimethylcyclopentadiene. In a 30-liter flask, 4.00 mole each of nitrogen chloride and of dimethylcyclopentadiene was irradiated by bright sunlight for 5 hours. The products obtained were 1,4-dichloro-4-nitrosodimethylcyclopentane (38 g., 0.315 mole, 38% conversion), 1,1,4-trichlorodimethylcyclopentane (63 g., 0.175 mole, 13.8% conversion), and an equal molar mixture of 1,4-dichlorodimethylcyclopentane and 1,3-dichlorodimethylcyclopentane (71 g., 0.187 mole, 18% conversion).

1,4-Addition to hexafluoropropene. In a 30-liter flask, a mixture of 2.37 mole each of hexafluoropropene and of nitrogen chloride was irradiated about 18 hours by bright sunlight. The products were washed and a small amount of tetrafluoroethane was obtained from the wash water. From the water insoluble portion there were obtained 1-trifluoromethylhexafluoropropene (14.4 g., 0.085 mole, 17% conversion), 1,2-dichlorohexafluoropropene (8 g., 0.076 mole, 9.3% conversion), and a solid material to which was assigned the structure 1-chloro-1-nitrosodifluoropropene.

another product of higher molecular weight was also obtained but not identified.

3. Addition to acetylacrylonitrile. In a 3-liter flask, 8.66 mole each of acrylonitrilebenzene and nitropl. chloride were irradiated for 8 hours. The products collected were 3-chloro-2-acrylonitrileacrylonitrile (3.8 g., 4.616 mole, 3% recovery), 3,7-dichloro-2-acrylonitrile (6.1 g., 1.033 mole, 3% recovery), and 3-chloro-2-acrylonitrileacrylonitrile (6.3 g., 8.666 mole, 4% recovery).

The blue nitro compound was identified by a comparison of its infrared spectrum with that of the nitro compound prepared from the addition to an olefinic chloride-chloroethyl formate system.

The dichloro compound was identified by a comparison of its infrared spectrum with that of an acrylonitrile sample.

The nitro compound had a strong infrared absorption at 6.8  $\mu$ , characteristic of the nitro group. Its nuclear magnetic resonance spectrum indicated that it was an equal mixture of  $\beta$ -nitropl. and 3-chloro-2-acrylonitrileacrylonitrile, i.e., 78-79% (area),  $\tau_{\text{CDCl}_3}^{\text{H}}$  2.301.

$\text{mp.}$  34.6,  $\text{bp.}$  47.4/0.5 mm.  $n_D^{20}$  1.335,  $n_D^{25}$  1.329.  $d_4^{20}$  1.030,  $d_4^{25}$  1.024.

5. Addition to trifluoroacrylonitrile. In a 3-liter flask, 6.733 mole of trifluoroacrylonitrile and of nitropl. chloride were irradiated for 8.5 hours. The mixture turned blue-green, indicating that a nitro compound had formed; however, only the following compounds were isolated: trifluoroacrylonitrile (6.3 g., 8.666 mole, 3.3% recovery), 1,3-dichloro-2-trifluoroacrylonitrile (1.4 g., 0.443 mole, 3% yield, 3% recovery), 1,7-dichloro-2-trifluoroacrylonitrile (6.1 g., 1.033 mole, 1.3% yield, 1.3% recovery), and 1-chloro-2-(2-chloro-2-nitro-2-trifluoroacrylonitrile) (1.6 g., 8.666 mole, 1% yield, 1% recovery).

The recovered olefins and the dihalides were identified by comparing their infrared spectra with those of known samples. 1,2-Dichloro-3-chloro-4-bromocyclohexene was identified by its infrared spectrum, and its structure was confirmed by nuclear magnetic resonance analysis. 1-Chloro-2-bromo-3-chloro-4-bromocyclohexene had a characteristic olefinic absorption at  $6.4\mu$  and a strong absorption at  $6.4\mu$  in the infrared. The nuclear magnetic resonance spectrum was consistent with that expected for the following structure:



The boiling point is  $87^\circ$  (unat.),  $n_D^{20}$  1.3703.

ANAL. Calcd. for  $\text{C}_6\text{H}_4\text{Cl}_2\text{Br}_2$ : Cl, 18.45; Br, 36.14. Found: Cl, 18.50; Br, 36.44.

5. Addition to 1,1-dichlorocyclohexene. The reaction was carried out in a 50-liter flask using 0.4 mole each of olefinyl chloride and 1,1-dichlorocyclohexene. After 3 hours of irradiation, some of the olefin was recovered unreacted. The following products were identified: 1,2-dichloro-3-chloro-4-bromocyclohexene (8.3 g., 0.043 mole, 10% conversion), 1,2-dichloro-3-chloro-4-bromocyclohexene (1 g., 0.005 mole, 4% conversion), 1,1,2-trichloro-3-bromocyclohexene (4 g., 0.015 mole, 1.5% conversion), 1,2-dichloro-3-chloro-4-bromocyclohexene and/or 1,1-dichloro-3-chloro-4-bromocyclohexene (1.5 g., 0.007 mole, 1.5% conversion). Also obtained were a little chlorocyclohexene and a white solid which was not identified.

6. Addition to 1,1-dichlorocyclohexene. A 3-liter flask was filled with 0.077 mole of olefinyl chloride and 0.077 mole of 1,1-dichlorocyclohexene. During 12 hours of sunlight irradiation the

glass retained brown. A colorless liquid gradually collected in the bottom of the flask. From this there were separated 2,4-dichloro-2,4-difluoro-1,3-dioxane (1.5 g., 0.007 mole, 18.4% conversion) and 2,4-dichloro-2,4-difluoro-1,3-dioxane-2-nitro compound (3 g., 0.017 mole, 58% conversion). The infrared spectrum of the nitro compound had a typical nitro group absorption at  $4.3\mu$ . Nuclear magnetic resonance analysis showed its structure to be [A] and that none of [B] was present:



[A]



[B]

The boiling point of [A] is  $118.2^\circ$  (atmos.),  $n_D^{20}$  1.3538.

ANAL. Calcd. for  $\text{C}_4\text{H}_2\text{Cl}_2\text{F}_2\text{NO}_2$ : Cl, 15.43; F, 6.43; N, 23.06.

Found: Cl, 15.47; F, 6.43; N, 23.76.

2. Addition to 1,3-dichloro-2,4-difluorodioxane. 1,3-Dichloro-2,4-difluorodioxane and nitrogen dioxide (0.008 mole each) were allowed to react for 1.5 hours. The color of the mixture turned to a brilliant, deep blue, and a small amount of blue liquid formed. 1,1,2-Trichloro-2,4-difluoro-1,3-dioxane was separated, b.p.  $80^\circ$  (atmos.),  $n_D^{20}$  1.406, molecular weight 197 (calculated for  $\text{C}_4\text{H}_2\text{Cl}_3\text{F}_2$  197.9). The infrared spectrum showed a typical absorption at 4.3  $\mu$  for the  $\text{NO}_2$  group.

ANAL. Calcd. for  $\text{C}_4\text{H}_2\text{Cl}_3\text{F}_2$ : Cl, 35.5. Found: Cl, 36.5.

#### General Procedure for the Addition of Nitrogen Dioxide to Dioxane

1. Evaluation of possible substrate materials. Each trial was carried out under identical conditions and in the same equipment. The reaction vessel was a 16 inch x 1.5 inch vertical glass tube with a gas

inlet tube extending almost to the bottom and ending in a coarse sintered glass surface. A gas outlet was provided near the top. In the bottom of the vessel there was a small magnetic stirrer. A heating tape wrapped around the tube maintained the temperature at  $50^{\circ}\text{C}$ . Nitrocellulose and chlorodifluoromethylene were filed out of their cylinders, and each was passed through a finely cleaned and calibrated flowmeter at a rate equivalent to 100 ml. air per minute. The gas streams were then combined and passed through the inlet tube of the reaction vessel and into a hot ( $50^{\circ}\text{C}$ ), stirred solution of 500 ml. toluene, chlorodifluoromethylene and 0.1 mole of the catalyst. In all trials the liquid volume amounted to about 1.5 per cent while the gases were passed through it. The products and unreacted starting materials distilled out of the reaction vessel and were led into a cold trap at  $-90^{\circ}\text{C}$ . An injection cap was placed between the reaction tube and the cold trap. Gas samples were taken before each trial and analyzed by vapor phase chromatography to insure an identical composition of starting materials each time. Gas samples were also taken at the vapors distilled out of the reaction tube 0.5 and 1.0 hours after the trial was begun, and vapor phase chromatographic analyses were made. The areas under each of the product peaks and the peak of unreacted chlorodifluoromethylene were measured and the results are tabulated in Table 4.

5. Evaluation of the rates of chlorine addition and chlorination. Four 15 ml. heavy-walled Pyrex tubes were filled on a vacuum line with the mixtures indicated in Table 5, sealed, and shaken for 6 hours in a dark closet. The tubes were then opened and the products separated preliminarily in a vacuum line and finally through a pyrochromatic scale gas chromatography column. Tube number 2 contained 0.20 g.



TABLE 4  
Catalyst Reductions

Catalyst	Time	area $\frac{H_2O}{H_2O+CO_2}$	area $\frac{H_2O}{H_2O+CO_2}$	area $\frac{H_2O}{H_2O+CO_2}$
$AlCl_3$	30 min.	5.60	0.779	—
	1 hr.	4.56	0.613	—
$AlF_3^{**}$	30 min.	0.296	0.109	0.133
	1 hr.	0.280	0.130	0.135
$Al_2(SO_4)_3^{**}$	30 min.	0.0313	—	0.0441
$BF_3 \cdot OEt_2$	30 min.	0.756	—	—
	1 hr.	0.513	—	—
$BaCl_2$	30 min.	—	—	0.0711
	1 hr.	—	—	0.0666
$CaF_2$	30 min.	0.0003	0.013	0.0770
$CaCl_2$	30 min.	0.0006	0.0009	0.130
	1 hr.	0.003	0.0013	0.164
$CaF_2$	30 min.	0.0116	0.0070	0.0006
	1 hr.	0.0763	0.0001	0.0030
$FeCl_2$	30 min.	0.0111	0.0009	0.135
	1 hr.	0.0083	0.0003	0.074
$FeCl_3$	30 min.	0.0039	—	0.0003
	1 hr.	0.0333	—	0.0166
$FeCl_2^{**}$	30 min.	0.167	—	—
	1 hr.	0.716	0.0043	0.0730
$HCl$	30 min.	0.0004	—	—
	1 hr.	0.0060	—	0.0026

TABLE 4 (continued)

Catalyst	Time	$\frac{\text{area } \text{HCO}^+}{\text{area } \text{C}_2\text{H}_5\text{CO}^+}$	$\frac{\text{area } \text{HCO}^+}{\text{area } \text{C}_2\text{H}_5\text{CO}^+}$	$\frac{\text{area } \text{HCO}^+}{\text{area } \text{C}_2\text{H}_5\text{CO}^+}$
LiF	30 min.	1.46	0.135	0.166
	1 hr.	0.474	0.0938	0.119
LiCl	30 min.	1.45	0.455	0.0003
	1 hr.	1.44	0.215	—
LiBr	30 min.	0.448	0.0409	0.0058
	1 hr.	0.007	0.0450	0.0040
LiBr <sub>2</sub>	30 min.	0.448	0.0058	0.007
LiF	30 min.	0.358	0.176	0.013
LiCl	30 min.	0.316	0.077	0.001
LiBr*	30 min.	0.305	0.0037	0.008
	1 hr.	0.0009	0.0006	0.003
LiCl**	30 min.	0.171	0.0007	0.0035
	1 hr.	0.003	0.0077	0.004
LiBr**	30 min.	0.068	0.0003	0.003
	1 hr.	0.173	0.0099	0.009
LiBr	30 min.	0.0401	0.0006	0.0000
	1 hr.	0.0073	0.0035	0.0038

\*  $\delta = 0.0001$ .

\*\* These values were only partially extractable in the solvent at 50°.

TABLE 5

Aluminum Spec for the Identification of  
the Sites of Aluminum Chloride and Diethylperoxide

Table No.	1	2	3	4
$\text{HCl}$ (1.0 ml., 0.06 mole)	+	+	+	+
$\text{CF}_3\text{COCl}$ (3.0 ml., 0.06 mole)	+	+	+	+
$\text{AlCl}_3$ (0.5 g., 0.0046 mole)		+		+
$\text{EtP}$ (0.6 ml.)			+	+

of nitrore, 3.8 g. of nitro, and 5.45 g. of nitro compound. Only traces of nitrotrifluoromethylene (estimated to be 0.0015 g.) and nitroaryl chloride (0.15 g.) were recovered. This number 4 contained slightly more of the nitro compound and about double the amount of nitro compound (4.30 g. and 4.35 g. respectively). The other tubes contained no nitro compound. This is interpreted to mean that aluminum chloride acts as the catalyst, and dimethylformamide acts only as a solvent.

Another tube containing nitrotrifluoromethylene (13.0 g., 0.1 mole), nitroaryl chloride (4.3 g., 0.1 mole), and aluminum chloride (5.3 g., 0.05 mole) was sealed and shaken 8 hours in the dark. After the tube had been opened and all volatile materials had been pumped off, 5.3 g. of a white powder remained which reacted vigorously with water, evolving heat and brown fumes. This material was apparently nitrobenzoyl nitro-ethylsuccinate (XV) and was obtained almost quantitatively.

#### Preparative Addition of Nitroaryl Chloride to Dimethylformamide-Catalyzed Reaction

In general, two sets of apparatus were used for additions to gaseous nitrore. (1) A 250 to 300 ml., ground flask was fitted with a mechanical stirrer, a gas inlet tube extending almost to the bottom of the flask, a 100-ml. vacuum sealed container, and a heating mantle. Nitroaryl chloride and dioxane were then bubbled into a warm, stirred mixture of aluminum chloride and dimethylformamide and refluxed for 2 to 4 hours. The products were then distilled out of the flask. (2) as 8 feet x 3/8 inch column was packed with 1/8 inch glass helices, wrapped with a heating tape, and inclined at about 15°. It was partially filled with a solution of aluminum chloride and dimethylformamide, and

through chloride and chloride were distilled into it at the same rate. Products were distilled out of the upper end of the column, bubbled through aqueous sodium bicarbonate solution, passed through a solution sulfuric drying tube, and finally condensed in a cold trap at  $-78^{\circ}$ .

1,3-Dichloro-4-chlorotrifluoromethane. In a 100-ml flask equipped as described above, one mole of chlorotrifluoromethylene and strong chloride were reacted in a mixture of chlorine chloride (75 g., 0.2 mole) and dimethylformamide (150 ml.). 1,3-Dichloro-4-chlorotrifluoromethane (200 g., 0.35 mole, 35% conversion) was obtained along with about 4 g. of 1,1,3-trichlorotrifluoromethane.

When the reaction was run in the inclined column described previously, the column was about three-fourths filled with a solution of chlorine chloride (66.25 mole) and dimethylformamide. Strong chloride (66.5 g.) and chlorotrifluoromethylene (75 g., 0.75 mole) were passed through the column at  $35^{\circ}$ , and 66.2 g. of the mixture composed 16.4 mole, 43% conversion) and 8.3 g. of dichloride (6.66 mole) were collected. The yield of chlorine material was actually higher than is reported here since some was still contained in the dimethylformamide solution, and no attempt was made to flush it out. Instead additional chloride (100 g. total) and strong chloride were passed through to produce a total of 88.5 g. of mixture composed and 34 g. of dichloride. When the dimethylformamide solution was finally drawn off and mixed with a large amount of water, 34 g. of 1,3-dichloro-4-chlorotrifluoromethane was obtained.

Using the apparatus described previously for the collection of acetylene materials, chlorotrifluoromethylene has been reacted almost quantitatively to a 98 per cent yield of the chlorine compound, 125 g. in about one hour.

2. Addition to hexafluoropropene. In a 3-necked flask equipped as previously described, hexafluoropropene (38 g., 0.38 mole) and nitroethyl chloride (13.5 g., 0.89 mole) were refluxed with a solution of aluminum chloride (39.7 g., 0.79 mole) and dimethylformamide (100 ml.). Benzene-d<sub>6</sub> per each of the flask was recovered and 1.8 g. of 1-chloro-2-nitroethanhexafluoropropene (3.634 mole, 39% yield) was obtained.

The same reaction was run in an isolated column as previously described using 81 g. of nitroethyl chloride and 43 g. of hexafluoropropene. Eighteen grams (40%) of the chloride was recovered, about 1 g. of 1,3-dichloroethanhexafluoropropene was obtained, and 26 g. (6.12 mole) of 1-chloro-2-nitroethanhexafluoropropene was obtained in 87 per cent yield and 86 per cent conversion.

The molecular weight of the nitro compound was determined by Legendre's method to be 315 (calculated for  $C_2H_2ClF_6NO_2$ , 315.35). The structure,  $CF_2HCFClNO_2$ , was confirmed by nuclear magnetic resonance analysis. The boiling point, determined kettlenormally, is 35°. The vapor pressure curve is described by the equation  $\log P = 6.55 - 4465/T$  over the temperature range -4 to +32°, the molar heat of vaporization is 6900 cal./mole, and the fusion constant is 33.4 cal./mole-deg.

ANAL. Calcd. for  $C_2H_2ClF_6NO_2$ : C, 14.75; H, 3.04; Found: C, 14.47; H, 3.04.

3. Addition to tetrafluoroethylene. No reaction was obtained on refluxing tetrafluoroethene-2 and nitroethyl chloride with a solution of aluminum chloride and dimethylformamide.

However, a reaction was obtained at 30 to 40° in an isolated column as previously described. Nitroethyl chloride (14 g., 0.38 mole) and tetrafluoroethene-2 (29.5 g., 1.19 mole) were passed through the heated

diethylformamide solution, and the olefin recovered by distillation of the washed condensate was recycled for a total of four passes. After the last pass, 40 g. (88%) of the olefin was recovered.

Thirteen grams (0.04 mole) of 3-ethoxy-4-methylpent-2-ene was obtained in 35.8 per cent yield and 94.5 per cent conversion. A very small amount of 4,5-dimethylpent-2-ene and 4.30 g. of 3-ethoxy-2-methylpent-2-ene were also obtained. The molecular weight of the olefin reported was determined by Rayleigh's method to be 84 (calculation for  $C_8H_{16}O$ , 84.1). The structure,  $CH_3CH(OCH_2CH_3)CH=CHCH_3$ , was confirmed by nuclear magnetic resonance analysis. The boiling point, determined barometrically, is  $56^\circ$ , and  $n_D^{20}$  is about 1.35. The vapor pressure curve is described by the equation  $\log P(0.35-1.35)/T$  over the temperature range  $+2$  to  $-31^\circ$ , the molar heat of vaporization is 7800 cal./mole, and the Trouton constant is 21.3 cal./mole-deg.

ANAL. Calcd. for  $C_8H_{16}O$ : C, 84.85; H, 10.15. Found: C, 84.14; H, 10.43.

The olefin used in the reaction was a mixture of  $\underline{g}_{12}$  and  $\underline{g}_{12}^{13}$  isotomers. The ratio of  $\underline{g}_{12}$  to  $\underline{g}_{12}^{13}$  isomer was determined by nuclear magnetic resonance analysis to be 1.8:1 before the reaction and 1.6:1 after the reaction. On this evidence it appears that the  $\underline{g}_{12}$  olefin is slightly more reactive than the  $\underline{g}_{12}^{13}$ . The olefin reported was obtained as an equal mixture of  $\underline{g}_{12}^{13}$  and  $\underline{g}_{12}$  isomers, also determined by nuclear magnetic resonance.

3,4-Dichloro-1,5-hexadiene ( $\underline{h}_{12}$  and  $\underline{h}_{12}^{13}$ ). In a column as previously described, hexamethylenes (40 g., 0.55 mole) and nitroyl chloride (10 g., 1.04 mole) were passed through a mixture of chlorine dioxide and diethylformamide at  $30$  to  $40^\circ$ . The molecular weight of the

nitrogen compound obtained was determined by Dumas's method to be 185 (calculated for  $C_{12}H_{11}F_3NO$  182; for  $C_{12}H_{11}ClF_3NO$  206.5), and an infrared spectrum of this material was identified to that of the nitrene compound prepared from the addition of nitrogen chloride to chlorotrifluoroethylene. The gases were obtained in 81 per cent conversion.

Adding the chlorotrifluoroethylene solution with a large amount of water caused some nitrene material to separate. Distillation of this gave 1.29 g. of 1,3-dichloro-3-nitrotrifluoroethane and 5.33 g. of what was assumed to be 1-bromo-3-chloro-3-nitrotrifluoroethane, b.p. 39°,  $n_D^{20}$  1.4015.

3. Addition to tetrafluoroethylene. In a flask equipped as previously described, nitrogen chloride (48 g., 0.334 mole) and tetrafluoroethylene (75 g., 0.36 mole) were reacted in a chlorotrifluoroethylene solution of aluminum chloride. The washed emulsion was separated by preparing the emulsion as chromatograph. 1,3-Dichloro-3-nitrotrifluoroethane (12.8 g., 26.3% conversion) was obtained along with 1.8 g. of 1,3-dichloro-3-bromotrifluoroethane.

Both of these structures were confirmed by elemental analysis. The molecular weight of the nitrene material was determined by Dumas's method to be 185 (calculated for  $C_2H_2F_3NO$  182), and the infrared spectrum was identified to that of the nitrene compound prepared from the addition of nitrogen chloride to chlorotrifluoroethylene.

5. Addition to hexafluoroethylene. This reaction was tried several times using a column reactor as previously described. In a typical trial, 78 g. of nitrogen chloride (0.55 mole) and 78 g. of hexafluoroethylene (0.448 mole) were put through the column. Nitrogen gas per cent of the effluent was measured, and 1,3-dichlorohexafluoroethane was



obtained in a 77% yield (8.811 mole).

2. Addition to p-trifluoromethylbenzotrifluoride. One and a half grams of p-trifluoromethylbenzotrifluoride was reacted with nitrogl chloride in a dioxylformamide solution of aluminum chloride. A green-colored mixture was obtained after 1.5 hours. The mixture was extracted with water to remove the dioxylformamide, and about 1 ml. of blue product was obtained. This was separated by gas chromatography into five components.

Component 1 was the blue p-(2-chloro-2-nitroethyl)benzotrifluoride, b.p. ca. 180 to 185° (lit.) with decomposition.

Anal. Calcd. for  $C_7H_4ClF_3NO_2$ :  $\bar{M}$ , 263.0;  $\bar{M}$ , 1.36. Found:  $\bar{M}$ , 261.6;  $\bar{M}$ , 1.43.

Component 2 was the known material p-(1,2-dichloroethyl)benzotrifluoride, b.p. ca. 190° (lit.),  $n_D^{20}$  1.433<sup>20</sup>. (Peters and Laffier reported b.p. 188/12,  $n_D^{20}$  1.4313 (41).

Component 3 was a clear compound and had a strong infrared absorption at 4.7  $\mu$ . It was assigned the structure  $CF_3$ - $CF_2CF_2CF_3$  rather than  $CF_3$ - $CF_3CF_2$  after comparing its infrared spectrum with those of p-(1,2-dichloroethyl)benzotrifluoride, p-(2-bromo-2-chloroethyl)benzotrifluoride, p-(2-bromo-2-chloroethyl)benzotrifluoride, p-(2-bromo-2-chloroethyl)benzotrifluoride and the starting olefin.

Components 4 and 5 were not identified.

3. Attempted addition to 1,2-dichloroethane/dichloro-2. The attempted addition of nitrogl chloride to 1,2-dichloroethane/dichloro-2 yielded only a small amount of 1,1,2,2-tetrachloroethane/dichloro-2. Most of the olefin was recovered.

4. Attempted addition to tetrahydrofuran. In reaction one

observed with tetrafluoroethylene. The catalyst was recovered unchanged. There was not even any evidence that chlorination had occurred.

20. Addition to Tetrafluoroethylene (21). In a typical reaction, approximately 8.4 mole of anhydrous  $\text{Cu}_2\text{O}$ , aluminum chloride dissolved in 150 ml. of reagent grade dimethylformamide was poured into a Pyrex tower 4 feet high and 1 inch in diameter. The tower was filled with 8 x 8 in. Raschig rings, then 8.85 mole of nitrogen chloride was dissolved in the solution. Tetrafluoroethylene, 8.46 mole, was bubbled through the tower from the glass dispersion tip at the bottom of the tower and stopped until there was no decrease in the amount collected in the liquid air trap at the end of the train. By using a slow flow rate the color of raschig rings of tetrafluoroethylene were held to a minimum. The solution in the tower was purged with nitrogen until no more blue gas distilled out. A chromatographic separation indicated a 48 per cent conversion and a 49 per cent yield of the desired 1-chloro-2-dichlorotetrafluoroethane substantiated by measured tetrafluoroethylene, and less than 18 per cent of 1,3-dichlorotetrafluoroethane with a small amount of higher boiling materials. The crude product was purified by distillation. By reducing the flow rate, conversions of about 70 per cent were obtained (20).

#### The Reduction of 1,3-Dichloro-2-dichlorotetrafluoroethane

The reduction was carried out under a very slow stream of nitrogen in a 125 ml. flask equipped with a stirrer, a dropping funnel, and an ice water condenser attached at its outer end to a Dry Gas-washer cooled trap. Nine grams of 1,3-dichloro-2-dichlorotetrafluoroethane and 7 ml. of 8 N hydrochloric acid were added to 25 ml. of refluxing diethyl

and 2½ g. of acid then. Almost immediately a blue crystalline formate near the top of the condenser and was slowly swept into the cold trap. When no further blue crystalline was observed, another 2 ml. of 6 N hydrochloric acid was added, and more blue material formed. Finally, 10 ml. of concentrated hydrochloric acid was added, and the reaction was stopped when no further blue material formed.

The blue material collected from the cold trap was examined by vapor phase chromatography and appeared to be mostly starting material along with 1,3-dichloro-3-nitroacetofluorenone (about 1 g., 10 to 15% conversion). The presence and structure of the nitron compound was confirmed by sealing the crude mixture in a tube with 1,2,3-trifluorobenzene. When the mixture turned colorless, it was distilled. The infrared spectrum of the fraction boiling at 38°/1 mm.,  $n_D^{20}$  1.4524, was identical to that of 3-[1,3-dichloro-3-nitroacetyl]-1,2,3,4-tetrafluoro-5,6-dihydro-1,2-naphthene, b.p. 15 to 38°/0.5 mm.,  $n_D^{19}$  1.4555 [4]. Nuclear magnetic resonance analysis further confirmed the product to be a pure sample of the above reaction.

#### The Reaction of Nitron Compounds with Nitron

In general, a heavy-walled Pyrex tube was constructed, sealed in the cold nitrogen, and charged with weighed amounts of the nitron compound and the nitron to be reacted. After being sealed, the tube was allowed to slowly warm up to room temperature. As indicated by the disappearance of the blue color of the nitron compound, the reaction was usually complete within an hour or two. The tube was opened into a vacuum line and the contents distilled. No low boiling products were found in any of the reactions.

1. Addition of 1-chloro-2,2-bis(4-chlorophenyl)propane to 1,1,1,2-tetrafluoroethane (2 g., 8.477 mols) and 2-chloro-2,2-bis(4-chlorophenyl)propane (3 g., 8.482 mols) were reacted as described. Distillation yielded a small bit of polymer and 2-(1-chloro-2,2-bis(4-chlorophenyl)-2,2,2-trifluoro-1,2-ethoxy)-1,2-propane (3.6 g., 8.81 mols, 85% conversion), b.p.  $37^{\circ}/15$  mm,  $n_D^{25}$  1.3915. The structure given was confirmed by nuclear magnetic resonance analysis.

Anal. Calcd. for  $C_{12}H_6Cl_6O$ : C, 38.17; Cl, 41.75; O, 20.08.  
Found: C, 38.18; Cl, 41.76; O, 20.06.

2. Addition of 1-chloro-2,2-bis(4-chlorophenyl)propane to 1,1,1,2-tetrafluoroethane. 1,1,1,2-tetrafluoroethane (0.8 g., 8.645 mols) and 2-chloro-2,2-bis(4-chlorophenyl)propane (3 g., 8.482 mols) were reacted. The products were a polymer and 2-(1-chloro-2,2-bis(4-chlorophenyl)-2,2,2-trifluoro-1,2-ethoxy)-1,2-propane (4.3 g., 8.613 mols, 95% conversion), b.p.  $37^{\circ}/15$  mm,  $n_D^{25}$  1.3916. The structure of the reaction was confirmed by nuclear magnetic resonance analysis.

Anal. Calcd. for  $C_{12}H_6Cl_6O$ : C, 38.17; Cl, 41.75; O, 20.08.  
Found: C, 38.18; Cl, 41.76; O, 20.06.

3. Addition of 1-chloro-2,2-bis(4-chlorophenyl)propane to 1,1,1,2-tetrafluoroethane. When the reaction was carried out as with other chlorine compounds, it resulted in a violent explosion about half an hour after the tube was removed from the liquid nitrogen bath. Examination of fragments of the glass tube revealed the inner side to be covered with black soot. The reaction was, however, successfully carried out by warming the tube from the liquid nitrogen bath to a dry ice-acetone bath and allowing this to slowly warm up to room temperature over a period of two days. Thus 1,1,1,2-tetrafluoroethane (2.38 g., 8.613 mols)

reacted with 3-nitropropylfluorosulfonate (1.9 g., 8.80E mols) to yield a small amount of polymer and 2-(2-pentafluoropropyl)-3,3,4-trifluoro-3,4-dichloro-4,4-tetraene (0.75 g., 8.80E mols, 4E converted),  $n_D^{20}$  1.365. The structure of the oxime was confirmed by nuclear magnetic resonance analysis. The infrared spectrum had an absorption at 3.6 $\mu$  for the  $\text{CF}_3\text{CF}_2$  group in addition to the absorption at 3.0 $\mu$  for the internal double bond,  $\text{=CF=CF=}$ .

ANAL. Calcd. for  $\text{C}_4\text{F}_8\text{Cl}_2\text{SO}$ :  $\bar{M}$ , 31.84;  $\bar{M}$ , 1.13;  $\bar{M}$ , 58.46;  $\bar{M}$ , 1.10. Found:  $\bar{M}$ , 31.41;  $\bar{M}$ , 1.14;  $\bar{M}$ , 58.39;  $\bar{M}$ , 1.13.

3. Addition of 1,2-dichloro-4-nitropropylfluorosulfonate to 1,1,2-trifluoro-2-chloroethane. 1,2-Dichloro-4-nitropropylfluorosulfonate (1.8 g., 8.8E mols) was reacted with 1,1,2-trifluoro-2-chloroethane (1.0 g., 8.8E mols). About 0.7 g. of the dimer was recovered, and essentially no polymer was formed. The product obtained was confirmed by nuclear magnetic resonance analysis to be 2-(2,2-dichloro-4-nitropropyl)-2-chloro-3,3,4-trifluoro-3,4-dichloro-4-tetraene (2.7 g., 8.80E mols, 8E converted),  $n_D^{20}$  1.404/1.5 m,  $n_D^{20}$  1.403.

ANAL. Calcd. for  $\text{C}_4\text{F}_8\text{Cl}_4\text{NO}_2$ :  $\bar{M}$ , 33.17;  $\bar{M}$ , 0.66;  $\bar{M}$ , 33.13. Found:  $\bar{M}$ , 33.13;  $\bar{M}$ , 0.65;  $\bar{M}$ , 33.06.

3. Addition of 1,2-dichloro-4-nitropropylfluorosulfonate to 1,1,2-trifluoro-2-chloro-3,4-dichloro-3-ene. Attempts to react 1,2-dichloro-4-nitropropylfluorosulfonate and 3,3,4-trifluoro-2-(2,2-dichloro-4-nitropropyl)-3,4-dichloro-3-ene in the usual manner resulted in a violent explosion. It was therefore necessary to cool the reactants in a tube at liquid nitrogen temperature and then to transfer the tube to a dry ice-acetone bath. The reaction appeared to be complete within a few hours as indicated by the disappearance of the blue color of the nitro compound. When the bath was allowed to warm

up to room temperature very slowly, the product polymerized and only a few mm remained.

8. Attempted addition of 1,2-dichloro-4-vinyl-2-fluorobenzene to 1,2-dichloro-3,4-difluorobenzene. 1,2-Dichloro-4-vinyl-2-fluorobenzene and 1,2-dichloro-3,4-difluorobenzene did not react over a ten day period at room temperature or at  $55^\circ$  over a period of one day. It did not seem advisable to heat the mixture for a longer period of time or at a higher temperature since under these conditions the dimerization of the diene compound becomes appreciable (49).

#### The Dimer of 1,2,3,4-dichloro-5-fluorobenzene-1,3,4-trifluoro-2,4-dichloro-1,3-diene

1,2,3,4-Dichloro-5-fluorobenzene-1,3,4-trifluoro-2,4-dichloro-1,3-diene (3.36 g., 8.44 mols) was refluxed for 8.5 hours in 15 ml. of  $n$ -pentane with  $\text{Zn}$ , 20 mg and a pinch of zinc chloride. No polymer product was evolved. The mixture was filtered, and the unreacted diene was washed with a little  $n$ -pentane. After removal of the solvent, reduced pressure distillation of the residue yielded only 8.45 g. of material, b.p.  $52^\circ/\text{mm.} \times \frac{20}{3}$  1.485. There was no recovered starting material. Paper phase chromatography indicated the product to be a mixture of two compounds in a molar ratio of 1:1.4. These were separated on a silicon column at  $100^\circ$ .

The first compound was assigned the structure 1-fluoro-2-chloro-7-fluorene. This structure is consistent with both the nuclear magnetic resonance and infrared spectra.

$\text{C}_{10}\text{H}_6\text{Cl}_2\text{F}_2$ . Calcd. for  $\text{C}_{10}\text{H}_6\text{Cl}_2\text{F}_2$ :  $\text{Cl}$ , 40.56;  $\text{F}$ , 31.14;  $\text{H}$ , 18.63. Found:  $\text{Cl}$ , 46.96;  $\text{F}$ , 31.83;  $\text{H}$ , 18.83.

The structure of the second compound could not be definitely

determined. It appeared to have one of the three structures shown below:



Either of these would appear to be consistent with the nuclear magnetic resonance and infrared spectra.

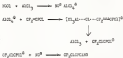
Calc. for  $\text{C}_{11}\text{H}_{19}\text{F}_5\text{O}_2$ :  $\text{Cl}$ , 36.46;  $\text{F}$ , 5.74;  $\text{O}$ , 12.66.

Found:  $\text{Cl}$ , 35.41;  $\text{F}$ , 4.24;  $\text{O}$ , 12.66.

## DISCUSSION

A study was made of the addition of nitroethyl chloride to a mixture of fluorobenzene in the presence of sunlight. With chlorobenzene-fluorobenzene it was observed for the first time that a mixture of two isomeric nitro compounds is produced: 1,1-dichloro-2-nitroethylfluorobenzene from the addition of nitroethyl chloride and 1,2-dichloro-2-nitroethylfluorobenzene from the disproportionation of 1,1-dichloro-2-nitroethylfluorobenzene.

A new method was developed for the addition of nitroethyl chloride to chlorine which involves the use of aluminum chloride as a catalyst and dichloroformate as a solvent. Other solvent and catalyst systems were investigated but were found to be less effective. The reactions with gaseous chlorine such as trichloroethylene or chlorotrifluoroethylene were carried out in a continuous process which could easily be adapted to large scale. Evidence is given to support the following suggested mechanism:





Another new route to chlorinated compounds was found which involves the reduction of the corresponding nitro compound.

Several chloroalkyl nitrate compounds were added to ketations, 1,1,3-trichlorobutadiene, 3-chloro-1,3,5-trichlorobutadiene, and 1,4-dichloro-2,3-diene-2-pyr. Reactions were obtained and the mechanism of the reaction is discussed. This is the first report of 3-chloro-1,1,3-trichlorobutadiene undergoing the Hunsdiecker reaction.

3-(1,3-dichloro-2-trifluoromethyl)-3,3,4-trifluoro-2,5-dihydro-2H-mexane was cleaved by n-pentane, and a preliminary investigation of the thermal decomposition of mexane is discussed.

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#### BIOGRAPHICAL SKETCH

Frank John Pizzarello was born February 18, 1930, in New York City. In October, 1948, he moved to Tampa, Florida. There, in June 1954, he graduated from Hillsborough High School. In June, 1958, he received the degree of Bachelor of Science in Geology from the University of Florida. In the following September, he began his graduate studies. He worked as a graduate, a teaching, and a research assistant until March, 1962, when he received the position of Postdoctoral Fellow which he has held until the present time.

Frank John Pizzarello is married to the Doctor Frances Eugenia Payer and has one son.

This dissertation was prepared under the direction of the chairman of the candidate's supervisory committee and has been approved by all members of that committee. It was submitted to the Dean of the College of Arts and Sciences and to the Graduate Council, and was approved as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

August 20, 1943

  
Dean, College of Arts and Sciences

  
Graduate Council

Supervisory Committee:

  
Chairman







  
for J. E. Schuyler